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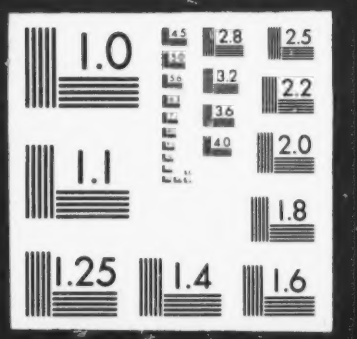

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CONTROL OF ENVIRONMENTAL HAZARDS IN WATER

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Environmental Protection Agency
Cincinnati, Ohio

7/8 June 1971

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SYMPOSIA ON ENVIRONMENTAL HAZARDS
ACS Third Central Regional Meeting
Cincinnati, Ohio
June 7-8, 1971

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CONTROL OF ENVIRONMENTAL HAZARDS IN WATER*

Jesse M. Cohen**

ENVIRONMENTAL HAZARDS

The production of pollutants and an increasing need for pollution management are inevitable concomitants of a technological society with a high standard of living. Pollution problems will increase in importance as our technology and standard of living continue to grow.

Huge quantities of diverse and novel materials are dispersed, from city and farm alike, into our air, into our waters and onto our lands. These pollutants are either unwanted by-products of our activities or spent substances which have served their intended purposes. By remaining in the environment they impair our economy, our health and quality of our life. They can be carried long distances by air or water, threatening the health, longevity, livelihood, recreation, cleanliness and happiness of citizens who have no direct stake in their production but cannot escape their influence.

Pollution affects human health and comfort in a number of ways. Under some circumstances, fortunately now rare, it brings overt clinical disease or even death. More commonly, however, it produces more subtle

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though damaging effects.

Only in recent years has the scientific community reacted to the small concentrations of hazardous material being discharged to the environment. Rivers no longer can accept the increasing pollution of metals, synthetic organics and pathogens and still serve the purposes of water supply and recreation. The apparently harmless concentrations can, by biological magnification become truly hazardous; witness the increases of metals and pesticides concentrations through the biologic food chain.

The variety and amounts of pollutants will not likely decline. The only options at the present time are to either contain the contaminants at their source or develop water and waste treatment processes which can cope with these pollutants. This paper discusses the capabilities of treatment processes to remove certain selected hazards from water.

WASTE TREATMENT PROCESSES

Biological

Over the past 40-50 years, and particularly within the past 10 years, waste treatment processes have been developed which have the capability of removing a wide variety of organic and inorganic contaminants. The problem is not so much the availability of processes so much as the lack of implementation. But new State and Federal regulations are providing the impetus to install the waste treatment capability we have now.

Except for primary plants which remove very little more than some suspended solids, the most common type of waste treatment plant is biological secondary treatment. Figure 1 describes the series of processes.

BIOLOGICAL TREATMENT SYSTEM

-Primary & Secondary-

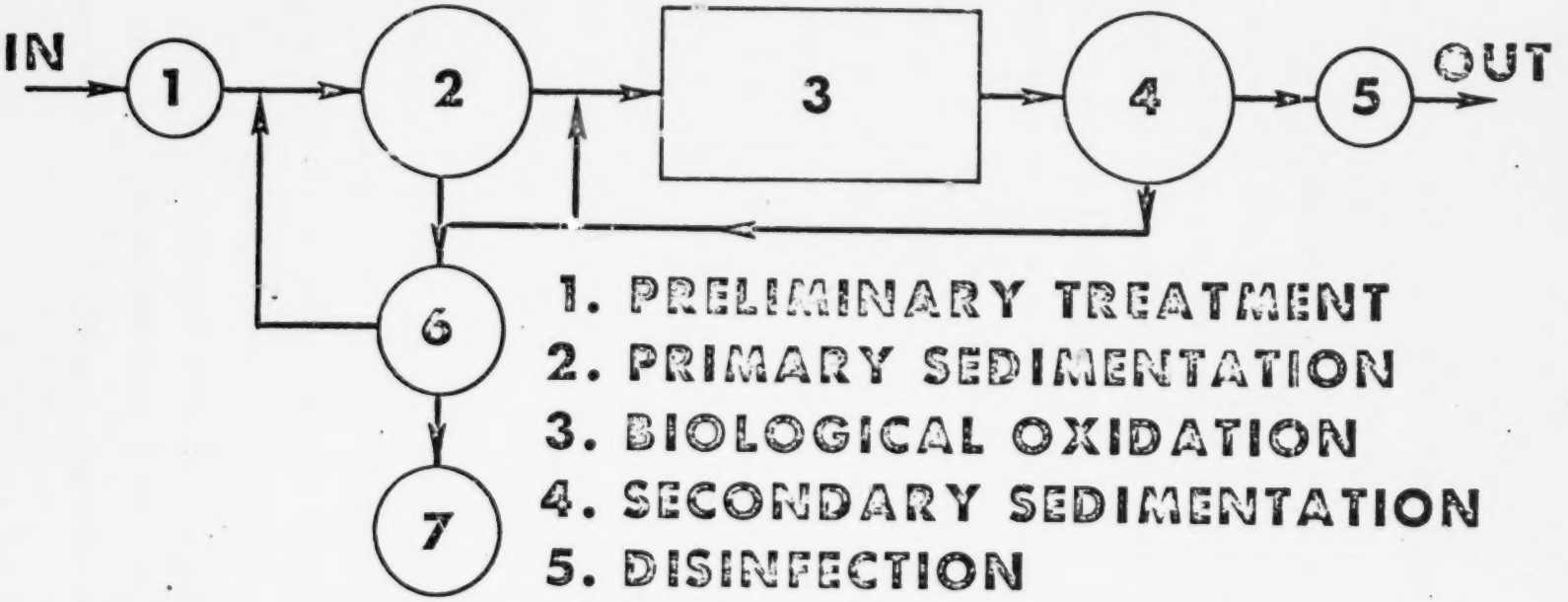

FIGURE 1

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After preliminary treatment which is designed to remove large objects and grit, the wastewater is settled in the primary tanks. At this point 60-70 percent of the suspended solids are removed. The settled solids are anaerobically digested, dewatered and disposed of by incineration or land burial. The overflow from the primary is treated by air aeration for 2-6 hours during which time degradeable organics disappear in the form of microbial cell mass, gases and energy. The sludge is settled in a final settler and disposed of. The clarified liquid, now low in organic content, is disinfected, usually by chlorine, and discharged.

Secondary biological plants have a capability of removing a variety of hazardous substances. Particulate material, as for example metal precipitates, will be removed by the primary settler. Organic materials, for example phenols, are substantially degraded to innocuous compounds in the aeration basin. Because of the large mass of organic material that is maintained in the aerator, certain pollutants, which do not degrade, for example pesticides, can yet be removed by adsorption. And finally, disinfection, if carefully done, can inactivate bacterial and viral pathogens.

The recent interest in removing phosphates from wastewaters has resulted in the development of processes which can accomplish this in existing secondary plants. Figure 2 illustrates essentially a biological treatment plant that has been modified to remove phosphates. Chemical precipitants such as iron or aluminum salts or lime can be added to either the primary or secondary tank. While this modification is designed to remove phosphates, an additional capability for removal of hazards is

BIOLOGICAL CHEMICAL TREATMENT SYSTEM

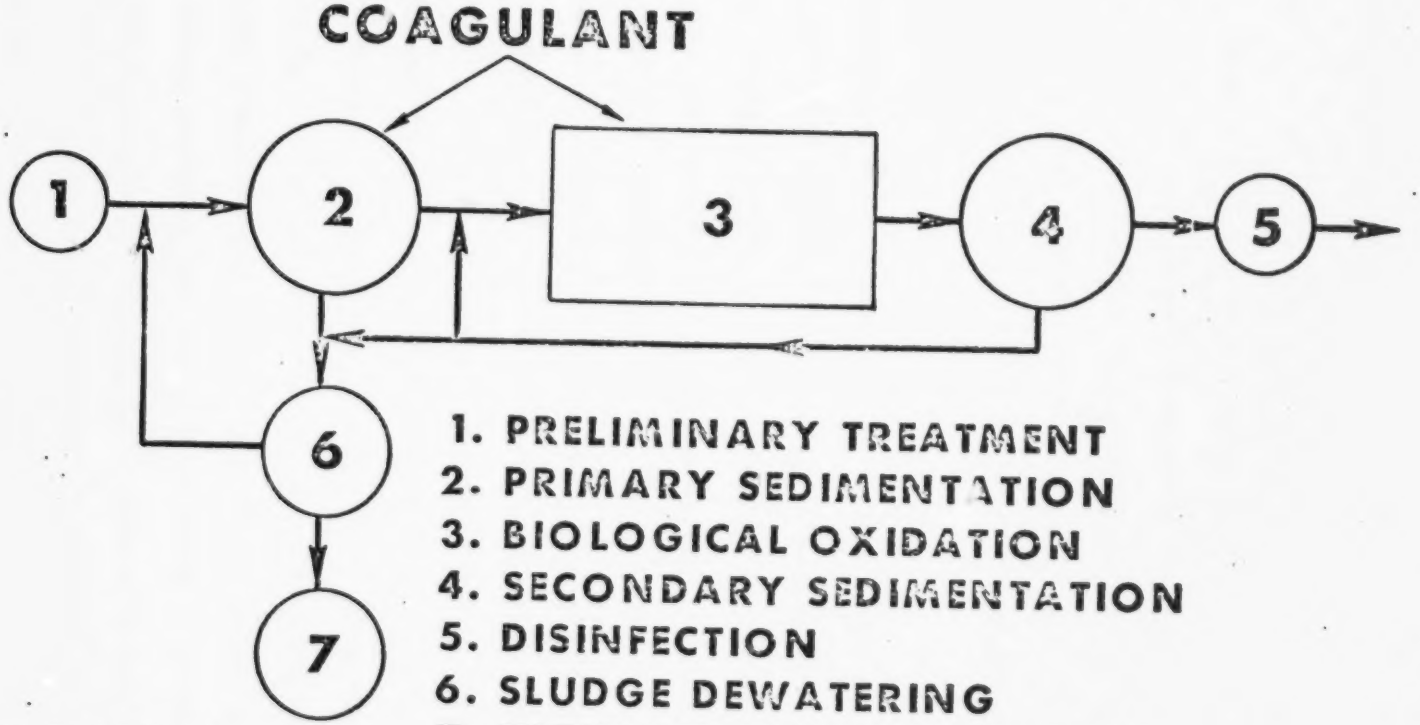

FIGURE 2

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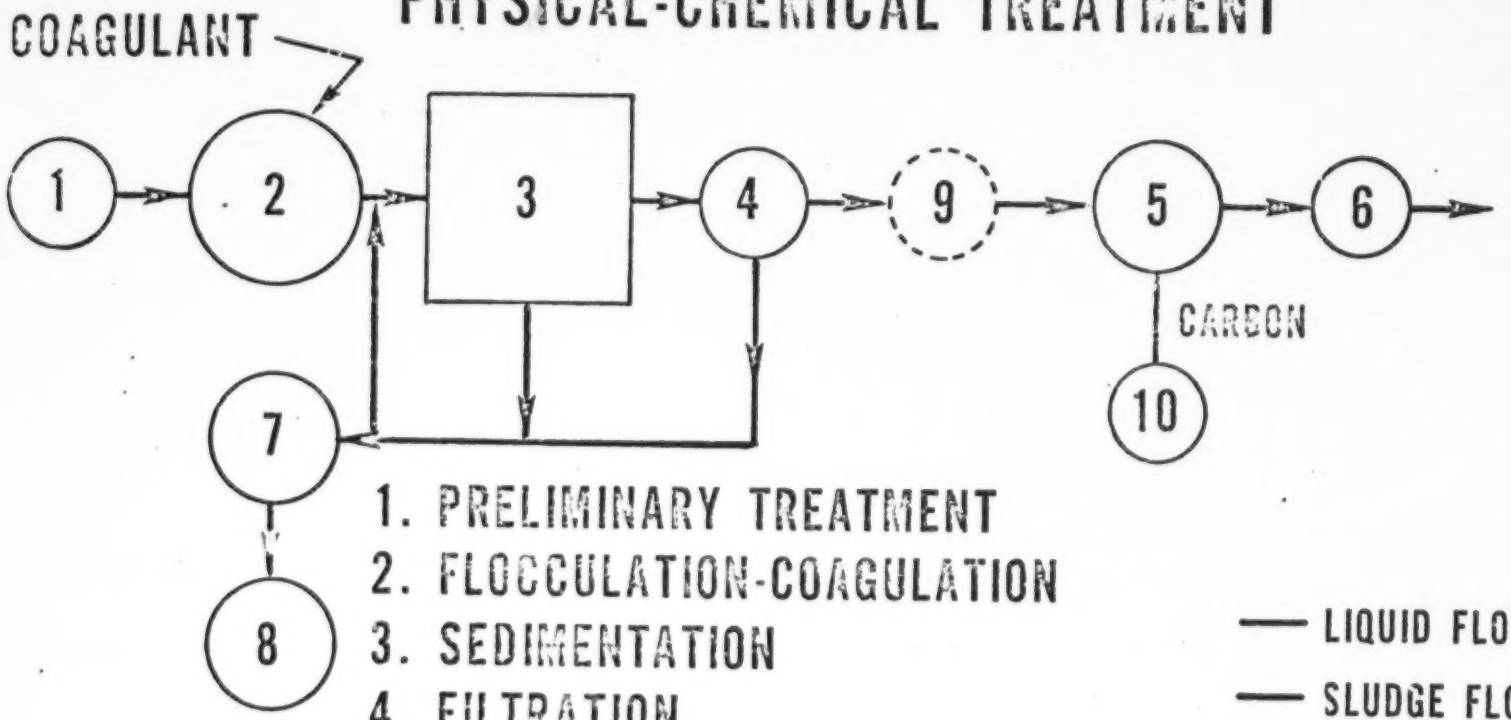
provided. As will be shown later, alum coagulation is an effective process for removal of heavy metals. Lime also removes metals but also inactivates viruses. But while the biological plant has been made more effective as a barrier to discharge of certain hazardous pollutants to the environment, it does not and cannot remove a large variety of non-degradeable organics which industry creates by the thousands each year.

Physical-Chemical

The most recent advance in the art of sewage treatment is the application of physical-chemical technology to raw sewage treatment. The system no longer depends on biological treatment for removal and, because of this, is uniquely capable of removing a wide variety of organic and inorganic contaminants. The system's capabilities can be adjusted to any desired efficiency by simply adding or omitting unit processes.

A flow scheme of a physical-chemical system is shown in Figure 3. After the usual preliminary screening and grit removal, chemical flocculants or precipitants are added to achieve clarification and phosphorus removal. The common chemicals are iron or aluminum salts, lime or organic polyelectrolyte. This unit process efficiently removes a large increment of pollutants as shown in Figure 4. Organic removal ranges from 70-80 percent, suspended solids in excess of 90 percent and phosphate removal ranges from 80 to as much as 98 percent. This unit process will remove much more than is indicated on the slide. Heavy metals are precipitated as the hydroxides or are adsorbed on the flocculated mass. The very large surface area also can adsorb dissolved organic substances, and finally, the high pH's

PHYSICAL-CHEMICAL TREATMENT



1. PRELIMINARY TREATMENT
2. FLOCCULATION-COAGULATION
3. SEDIMENTATION
4. FILTRATION
5. CARBON ADSORPTION
6. DISINFECTION
7. SLUDGE DEWATERING
8. ULTIMATE DISPOSAL
9. OPTIONAL NITROGEN REMOVAL
10. CARBON REGENERATION

— LIQUID FLOW
— SLUDGE FLOW
— CARBON FLOW

FIGURE 3

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TECHNICAL TEMPLATE
TECHNICAL TEMPLATE
TECHNICAL TEMPLATE

ACHIEVEMENTS OF CHEMICAL CLARIFICATION

PLANT	CHEMICAL	ORGANIC REMOVAL %	SS REMOVAL %	P REMOVAL %
EWING-LAWRENCE	170 mg/l $FeCl_3$	80	95	90
NEW ROCHELLE (ZM)	LIME pH 11.5	80	98	98
WESTGATE,VA.	125 mg/l $FeCl_3$	70	-	-
SALT LAKE CITY	80-100mg/l $FeCl_3$	75	-	80
BLUE PLAINS	LIME pH 11.5	80	90	95

FIGURE 4

normally a part of lime precipitation can hydrolyze organics and inactivate viruses.

Returning to Figure 3, the solids resulting from the precipitation are dewatered and disposed by incineration or burial. Spreading of lime sludge on land is also feasible. The overflow from the precipitator is filtered through a deep bed of either sand or sand-coal mixture to remove solids which evaded capture in the clarifiers.

The filtrate is then treated by activated carbon adsorption, which has as its principal function the removal of dissolved organics. The product, now fully clarified and low in organic content, can be readily disinfected. When the activated carbon is exhausted, it is regenerated thermally at temperatures of 1600-1700°F. This is important. Hazardous organic substances which adsorb are incinerated to gaseous end-products which are scrubbed from the furnace stack.

Activated carbon is a most unique material which is capable of removing a wide range of pollutants, organics, metals and virus particles. The organic removal capability of the system - coagulation-carbon-adsorption - is shown in Figure 5. Removals in excess of 95 percent have been achieved at four experimental plants shown here. An imponderable here in terms of hazardous materials, is the identification of the residual organic material that still remains in the product water. Organic content of 3-11 mg/l of total organic carbon is still in excess of that found in clean waters. Should removal of this final trace of organics be necessary, oxidation processes such as ozonation may be useful. Ozonation is being investigated.

TOTAL TREATMENT P-C PLANTS

PLANT	ORGANIC REMOVAL %	EFFLUENT CONCENTRATION
BLUE PLAINS	95-98	TOC=6
LEBANON	95	TOC=11
EWING-LAWRENCE	95-98	TOC=3-5
NEW ROCHELLE	95	COD=8

FIGURE 5

REMOVAL OF HAZARDOUS POLLUTANTS

We know that thousands of synthetic organic and inorganic pollutants, some clearly hazardous to human and biological life are being discharged to wastewaters; yet very little hard information has been developed on the treatability of these pollutants. We can make educated guesses about what the various unit processes may do, but we cannot be sure until each pollutant is empirically studied with each process; and this information is sorely lacking. In this paper, I will discuss four general classes of potentially hazardous compounds: heavy metals, carcinogens, pesticides, and virus.

Heavy Metals

Heavy metals enter our streams from a variety of sources, some from man's activities, others from natural geologic processes. Mine drainage, because of its high acidity, dissolves large quantities of metals from the surrounding mineral environment. The metal working industry discharges, frequently directly to the sewer, large quantities of hazardous metals such as zinc, copper, chromium, lead, cadmium, and others.

Physical-chemical treatment, which employs chemical precipitation for clarification and phosphate removal is an effective process for metals removal. In Figure 6 are the calculated solubilities of some metals at various pH's. The normal pH range of sewage is about 6.5 to 8.0, and at these pH's it can be seen from this table that copper and ferric iron are essentially insoluble. Ferrous iron and zinc require a pH of at least 10 to precipitate out to any major degree. Lime treatment is

CONCENTRATION OF IONS

mg/l

pH	Cu^{++}	Fe^{+++}	Fe^{++}	Mn^{++}	Zn^{++}
2.0	-	6.2×10^{4}			
3.0	-	6.2×10^{1}			
4.0	9.6×10^{4}	6.2×10^{-2}			
5.0	9.6×10^{2}	6.2×10^{-5}			
6.0	9.6×10^{0}				
7.0	9.6×10^{-2}		9.2×10^{4}		1.2×10^{5}
8.0	9.6×10^{-4}		9.2×10^{2}		1.2×10^{3}
9.0			9.2×10^{0}		1.2×10^{1}
10.0			9.2×10^{-2}		1.2×10^{-1}

HIGHLY INSOLUBLE

HIGHLY SOLUBLE

FIGURE 6

generally practiced at pH's 10 to 11.5 and will therefore ensure that all the metals shown will be effectively insolubilized.

Wastewaters, on standing, rapidly become anaerobic and generate hydrogen sulfide. Sulfides are present in both biological and physical-chemical treatment. A comparison of the solubilities of the sulfides and hydroxides of metals, as illustrated in Figure 7, shows that metal concentrations can be reduced to vanishingly small concentrations by precipitation as the metal sulfide. Precipitation of the metals, of course, transfers the problem from the liquid to the sludge. When properly disposed of by burial or by incineration followed by burial of the ash, the metals are immobilized and should pose no threat to the environment.

Some recent experimental evidence confirms the above predictions of metal removal. Alum is commonly used for clarification and to precipitate phosphates. The process is also effective in removing certain metals. The data are shown in Figure 8. In bench scale tests, 100 mg/l of alum was added to wastewater which had been spiked with various metals to a concentration of about 3 mg/l. It can be seen that lead, copper and chromium (III) are reduced to less than 1 mg/l. Cadmium, arsenic, chromium (VI) and zinc are only partially removed. Predictably, lime is much more effective in removing metals. These data are shown in Figure 9. All metals with the exception of chromium (VI), are reduced to less than 1 mg/l. In this test, lime was added to only pH 9.5 whereas more usual practice is to raise the pH to 10-11.5 where even better removals would be

SOLUBILITY OF METAL HYDROXIDES AND SULFIDES

METAL	HYDROXIDE	SULFIDE
Cu	1.5×10^{-20}	8.5×10^{-45}
Fe(II)	1.6×10^{-14}	3.7×10^{-19}
Fe(III)	1.1×10^{-36}	-
Mn	4.0×10^{-4}	1.4×10^{-15}
Zn	1.8×10^{-14}	1.2×10^{-23}

FIGURE 7

PRECIPITATION OF METAL IONS IN WASTEWATER BY ALUM(A)

	METAL PRESENT MG/L	METAL REMAINING MG/L	REMOVAL %
Pb(II)	4.0	0.5	86
Cu(II)	3.3	0.2	94
Cd(II)	3.1	1.4	55
As(V)	4.2	1.2	72
Cr(III)	3.3	0.4	88
Cr(IV)	3.0	2.3	23
Zn(II)	2.6	1.7	35

(a) ALUM DOSE - 100 mg/l pH 6.5-7.0

PRECIPITATION OF METAL IONS IN WASTEWATER BY LIME (a)

	METAL PRESENT mg/l	METAL REMAINING mg/l	REMOVAL PERCENT
Pb(II)	4.0	0.3	93
Cu(II)	3.3	0.2	94
Cd(II)	3.1	0.2	94
As(V)	4.2	0.6	86
Cr(III)	3.3	<0.1	>97
Cr(IV)	3.0	3.0	0
Zn(II)	2.6	0.2	92

(a) LIME AT pH 9.5

FIGURE 9

obtained. The small residuals of metals remaining after precipitation may be further reduced by adsorption on activated carbon but experimental evidence is lacking.

Carcinogens

There is mounting evidence that polycyclic hydrocarbons, some of which are carcinogenic, are ubiquitous in our environment. Many investigators believe that carcinogens do not have a threshold or safe limit of concentration so that even the slightest concentration of the substances exerts an irreversible effect on man. Nevertheless, it has been proposed that, for man, a safe concentration of 3,4-benzpyrene in water is $3x10^{-5}$ mg/l or 0.03 parts per billion. Clearly, to be effective, waste treatment must accomplish virtually total removal of these substances.

Modern society generates carcinogenic hydrocarbons in many of its activities. Much of these materials find their way into water courses. A review of the occurrence of polycyclic hydrocarbons reveals that they have been found in wastewaters at concentrations of 1-100 ppb, in surface waters at 0.01-1 ppb and even in ground water at 0.001-0.01 ppb. The wastewater from certain industrial operations such as coke plants and oil refining can range from 30 to 300 ppb of 3,4-benzpyrene.

I am not aware of any direct evidence that sewage treatment processes remove polycyclic hydrocarbons, but indirect evidence suggests that physical-chemical treatment would effectively remove these substances. Activated carbon, which is part of a physical-chemical system, has been shown to be an effective adsorbent for polycyclics. For example, an examination of a

benzene extract of carbon which had been used to treat Rhine River water showed that 0.1 mg of polycyclics was present per kilogram of dry carbon.

Chemical oxidation is an effective process for removing the hazards of polycyclics. Chlorine, when used in the usual dosages and contact times for disinfection, was not effective, but 1 mg/l of chlorine dioxide with a contact time of about 60 minutes achieved a 90 percent reduction of benzpyrene. Interestingly, seven reaction products were identified and were shown no longer to be carcinogenic.

By far the best oxidant is ozone. In distilled water 1-100 µg/l of benzpyrene could be oxidized to the extent of 99 percent by ozonation with 0.5-1.5 mg/l ozone. The reaction product was believed to be an inactive compound, 8 hydroxy-3,4-benzpyrene. The results of ozonation of some polycyclic hydrocarbons are shown in Figure 10. Aqueous solutions of the indicated polycyclic hydrocarbons were treated with 400 mg/l of ozone for contact times of 1 to 10 minutes. All hydrocarbons were found to be inactivated by contact with ozone for 2-1/2 minutes. The percent remaining after 1 minute contact is shown in the tabulation. Pyrene and 3,4-benzpyrene appear to be more resistant to ozone.

While ozone is not now commonly used in wastewater treatment it is being investigated for use both as an alternative to chlorine for disinfection and as an alternative or supplement for carbon adsorption. In either case, ozone will provide an effective treatment for polycyclic hydrocarbons.

OZONATION OF POLYCYCLIC HYDROCARBONS

HYDROCARBON	% REMAINING
3,4-BENZPYRENE	39
PYRENE	15
1,2-BENZANTHRACENE	4.5
1,2,5,6-DIBENZATHRACENE	3.6
9,10-DIMETHYL- 1,2-BENZANTHRACENE	0

(a) INITIAL CONCENTRATION 6.7 μg/l
(b) OZONE CONCENTRATION 400 mg/l
(c) CONTACT TIME 1 MINUTE
(d) ALL HYDROCARBONS INACTIVATED IN 2½ MINUTES

FIGURE 10

Pesticides

The problem of pesticides in the environment has been adequately described in many publications. Very little work, however, has been done on evaluating the effectiveness of various processes in removing these pollutants. One study, published in 1965, determined the effectiveness of water treatment processes in removing selected pesticides. Figure 11 summarizes the cumulative removals of 10 ppb of pesticide by chlorination, coagulation-filtration and granular carbon adsorption. Chlorination is clearly ineffective. Alum coagulation is quite effective for the more insoluble pesticides like DDT and 2,4,5-T butoxy ethanol ester, but is only partially effective for the others. The process which is most effective is granular activated carbon. Activated carbon is a key process in physical-chemical treatment, as discussed earlier, and should be effective in the removal of pesticides from wastewater. Most pesticides adsorb readily on surfaces, and since wastewater treatment, whether biological or physical-chemical, invariably involves masses of solids, it is not surprising that pesticides are removed by treatment. What really happens, is that the small concentration in the raw sewage is concentrated into the sludge. For example, an analysis of incoming sewage showed a DDT concentration in the low ppb level, but the sludge contained up to 60 ppm of DDT and its metabolites. Disposal of this sludge must now consider this substantial DDT concentration.

CUMULATIVE PESTICIDE REMOVAL FROM RIVER WATERS

PROCESS	PESTICIDE REMOVED - PERCENT			
	DDT	LINDANE	DIELDRIN	2,4,5-T ESTER
CHLORINATION - 5 mg/l	<10	<10	<10	<10
COAGULATION-FILTRATION	98	<10	55	65
GRAN. ACTIVATED CARBON	>99	>99	>99	>99

FIGURE 11

Virus

Human disease-producing virus can always be isolated from raw sewage. But since virus do not multiply outside of susceptible living cells, their numbers decline when discharged to the environment; but not so fast that they cannot be detected in rivers below waste treatment plants that do not practice disinfection. A major barrier to virus contamination of rivers is, of course, disinfection. But with poorly treated sewage containing ammonia and suspended particles, the disinfection process is imperfect and virus particles persist.

Flocculation of raw sewage with lime, another of the key processes in physical-chemical treatment, has been shown to be effective in inactivating virus. Flocculation alone, as for example with iron or aluminum salts and lime at low pH's, will remove up to 99 percent of the virus. But this, clearly, is not good enough.

Lime precipitation for clarification and phosphate removal, is frequently practised at pH 11.3-11.5, as at Lake Tahoe. At these pH's almost total removal of virus is obtained. Removal is obtained both by physical adsorption and entrapment in the flocculating mass and by the effect of high pH. The overall effect is shown in Figure 12. In this study, poliovirus I was added to secondary effluent, and then flocculated with lime dosages varying from 200 to 500 mg/l. The resulting pH's ranged from 9.27-11.20. Samples for virus recovery were obtained after settling and filtration through a bed of sand. This test shows that lime treatment at a pH less than about 10.8 does not adequately remove virus. The

REMOVAL OF POLIOVIRUS BY LIME PRECIPITATION AND SAND FILTRATION

FINAL pH	VIRUS REMAINING pfu/1[(a)]	VIRUS REMOVED %
9.27	336	99.0
10.13	685	98.7
10.88	1.7	99.995
11.10	5.1	99.98
11.20	<1.4	>99.997

(a) INITIAL CONCENTRATION OF VIRUS 33,000 TO 55,000 PFU/1

percentage removal is high but the virus remaining is also too high. Above pH 10.8 and certainly at the commonly used pH's of 11.3-11.5, very high virus removals are obtained. Lake Tahoe which practices lime treatment at about pH 11.5 followed by chlorine disinfection has never been able to isolate virus in their product.

SUMMARY AND CONCLUSION

Most waste treatment processes, both biological and physical-chemical have been developed to meet such common gross parameters as BOD, DO, pH, phosphates, nitrogen, etc. Almost unwittingly, the processes developed to meet the usual water quality requirements, have turned out to be remarkably capable of removing a wide range of hazardous substances. The chemical processes of biological oxidation, chemical precipitation, adsorption and disinfection, in combination, are a formidable barrier to a wide variety of environmental hazards. This paper has presented evidence that heavy metals, polycyclic hydrocarbons, insecticides and virus can be effectively reduced or totally removed from wastewater.

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